occasionally being as much as 0.3 v. This, together with the fact that Lingane found only a single thermodynamically reversible wave over the *p*H range he studied (but compare his curve c, Fig. 1), suggests that the gelatin exerts a considerable effect on the rates of the reactions occurring in the solution and at the drop surface. Some such interpretation seems to be demanded also by the discrepancy between Lingane's report that solutions of iron(III) in 0.5 *F* citrate containing 0.005% gelatin were colorless at *p*H values above about 10 and the finding in the present work that similar solutions containing no gelatin were still pale yellow when precipitation of hydrous ferric oxide began at *p*H 12.5 in 0.5 *F* citrate and *p*H 11.7 in 0.12 *F* citrate.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE PAINT DIVISION OF THE PITTSBURGH PLATE GLASS COMPANY]

The Molybdate-catalyzed Hydrogen Peroxide Oxidation of β-Naphthol

BY ALFRED R. BADER

The red compound, m.p. 148°, isolated by Raacke-Fels, *et al.*,[1] in the molybdate-catalyzed hydrogen peroxide oxidation of β-naphthol has been shown to be 4-(2′-hydroxy-1′-naphthyl)-1,2-naphthoquinone.

During studies on the influence of molybdates on hydrogen peroxide oxidations, Raacke-Fels, *et al.*, discovered[1] that β-naphthol was oxidized in the presence of a catalytic amount of ammonium molybdate in a mixture of ethanol, acetic acid and water to a red compound, m.p. 148°, soluble in aqueous carbonate but insoluble in bicarbonate. Raacke-Fels, *et al.*, showed the molecular weight of this compound to be about twice that of β-naphthol, but examined it no further and assigned no structural formula to it.

In the present investigation, it was found that solutions of this red oxidation product of β-naphthol, of empirical formula $C_{20}H_{12}O_3$, were decolorized by alkaline hydrosulfite in the cold, and that it reacted easily with *o*-phenylenediamine in acetic acid to form a yellow monophenazine, $C_{26}H_{16}ON_2$, m.p. 293–294°, which acetic anhydride and sodium acetate converted to a phenazine monoacetate, $C_{28}H_{18}O_2N_2$, m.p. 181–182°. Thus is appeared that β-naphthol had dimerized in the molybdate-catalyzed oxidation, and that one of the β-naphthol moieties had become oxidized to a 1,2-quinone system. That this is correct was confirmed by the ultraviolet spectrum of the red oxidation product (Fig. 1) which is perfectly explained by summation of the spectra of non-coplanar[2] β-naphthol[3] and 1,2-naphthoquinone.[4]

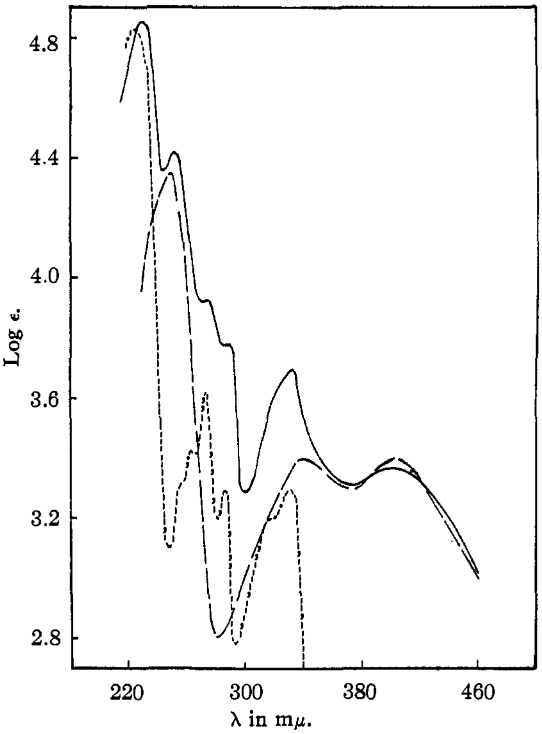
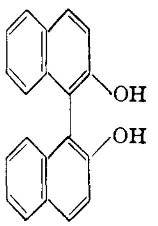
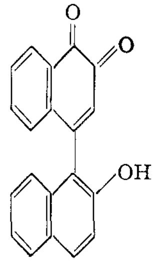


Fig. 1.—Absorption spectra in absolute ethanol of 4-(2′-hydroxy-1′-naphthyl)-1,2-naphthoquinone (II), ——; β-naphthol, - - - - -; and 1,2-naphthoquinone, — —.

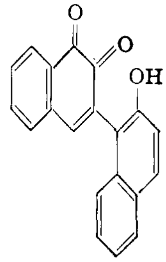
Dimerization of β-naphthol yields β-dinaphthol (I) which oxidation could not convert into a hydroxy-1,2-naphthoquinone, and so oxygenation of β-naphthol must precede dimerization. 1,2-Naphthoquinone and its hydroquinone couple at positions 3 and 4,[5,6] and thus II and III are the possible formulations of the monoquinonoid dimer of β-naphthol. Peracetic acid oxidation distinguished between these unambiguously, as it yielded 4-(2′-carboxyphenyl)-5,6-benzcoumarin(IV) which has been synthesized[7] by the condensation of β-naphthol and phthalylacetic acid. This coumarin had been isolated previously in both the alkaline permanganate[7,8] and the molybdate-catalyzed peracetic acid[1] oxidations of β-naphthol, and II may be an intermediate in these oxidations. The identity of the peracetic acid oxidation product of the quinone II and the coumarin synthesized by the elegant method of Dischendorfer and Danziger was established by melting point, mixed melting point, iden-



I



II



III

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[5] S. C. Hooker and L. F. Fieser, THIS JOURNAL, **58**, 1216 (1936).

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[8] E. Ehrlich, *ibid.*, **10**, 115 (1889).

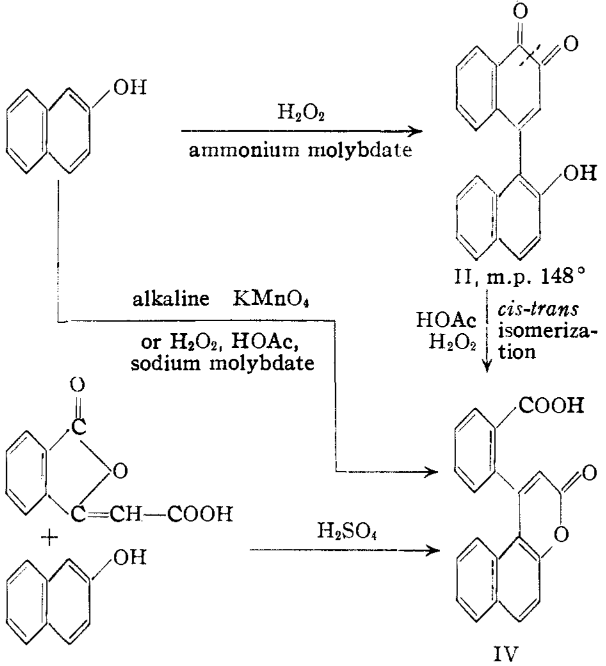
TABLE I

ULTRAVIOLET ABSORPTION SPECTRA IN ABSOLUTE ETHANOL[a]

Compound	Absorption maxima, wave lengths in mμ, log ε values					
β-Naphthol[3]	226 (4.83)		274 (3.63)	286 (3.30)	331 (3.30)	
1,2-Naphthoquinone[4]		250 (4.35)			340 (3.40)	405 (3.40)
4-(2'-Hydroxy-1'-naphthyl)-1,2-naphthoquinone	230 (4.86)	252.5 (4.42)	274.5 (3.92)	288 (3.78)	332.5 (3.70)	405 (3.37)
4-(2'-Carboxyphenyl)-5,6-benzcoumarin	229 (4.70)				320 (3.95)	351 (4.03)
4-(2'-Carbomethoxyphenyl)-5,6-benzcoumarin	230 (4.74)				320 (3.93)	352 (4.02)
3-Bromo-4-(2'-carboxyphenyl)-5,6-benzcoumarin	228 (4.69)				325 (4.01)	357.5 (4.14)

[a] Thanks are due to Miss Merle Manchester for conducting the spectrographic determinations.

tical ultraviolet spectra and the preparation of identical methyl esters and monobromo derivatives from both.



Experimental

4-(2'-Hydroxy-1'-naphthyl)-1,2-naphthoquinone (II) prepared by the method of Raacke-Fels, *et al.*,[1] was dissolved in a minimum of glacial acetic acid; the solution was filtered to remove a small quantity of an orange impurity, and the quinone was precipitated by the addition of a concentrated sodium chloride solution and recrystallized several times from aqueous acetone, m.p. 148–149°. The yield from 1 g. of β-naphthol was 0.7 g. (67%).

Anal. Calcd. for $C_{20}H_{12}O_3$: C, 79.98; H, 4.03. Found: C, 79.69, 79.58; H, 4.28, 4.30.

The **phenazine**, prepared by condensation of the 1,2-quinone (II) with *o*-phenylenediamine in acetic acid, formed yellow needles from ethanol, m.p. 293–294°.

Anal. Calcd. for $C_{26}H_{16}ON_2$: C, 83.85; H, 4.33; N, 7.52. Found: C, 84.17, 84.03; H, 4.66, 4.71; N, 7.57, 7.47.

The yellow **phenazine acetate**, prepared by refluxing the phenazine with acetic anhydride, glacial acetic acid and sodium acetate and crystallized from aqueous ethanol, melted at 181–182°.

Anal. Calcd. for $C_{28}H_{18}O_2N_2$: C, 81.14; H, 4.38; N, 6.76. Found: C, 81.33; H, 4.80; N, 6.72.

4-(2'-Carboxyphenyl)-5,6-benzcoumarin (IV).—A solution of 3.2 g. of the quinone II in 120 cc. of glacial acetic acid and 20 cc. of 20% aqueous hydrogen peroxide was allowed to stand at room temperature for 40 hours. The resulting yellow solution was poured into water, and the light cream precipitate (2.3 g.) was filtered, dried and crystallized with charcoal from ethanol to yield 1.8 g. (53%) of almost white, shiny platelets, m.p. 278–279°, which did not depress the m.p. of the coumarin prepared by the sulfuric acid condensation of β-naphthol and phthalylacetic acid.[7]

The monobromides,[7] m.p. 250–252°, prepared from the oxidation product and the synthetic coumarin were identical.

4-(2'-Carbomethoxyphenyl)-5,6-benzcoumarin, prepared by the action of diazomethane[9] on a solution of the acid in a mixture of ether and methanol, formed faintly yellow, stout needles, m.p. 153–154°, identical with the ester prepared by the method of Dischendorfer, *et al.*[7]

Anal. Calcd. for $C_{21}H_{14}O_4$: C, 76.35; H, 4.27. Found: C, 76.23; H, 4.40.

Acknowledgment.—The author wishes to thank Drs. H. L. Gerhart, S. W. Gloyer and H. A. Vogel for their interest in this work, and Dr. M. G. Ettlinger, whose many valuable suggestions speeded the solution of this problem.

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(9) Prepared by the convenient method of A. F. McKay, THIS JOURNAL, **70**, 1974 (1948).